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# Stereoselective synthesis of arenechromium tricarbonyl complexes: Origins of the benzylic oxygen directing effects for 1-tetralol derivatives

**Stephen G. Davies* and Craig L. Goodfellow**

*The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY (Great Britain)*

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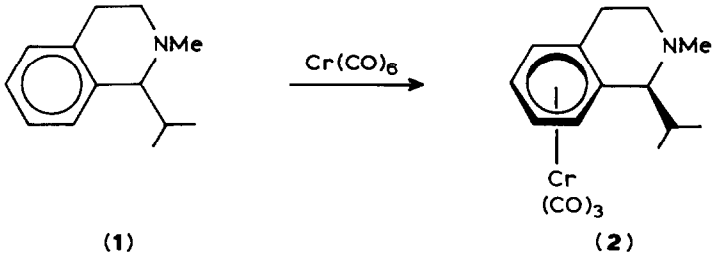
## Abstract

Thermolysis of chromium hexacarbonyl with 1-tetralol (**10**) or 1-methoxytetralin (**12**) yields the corresponding *syn*-chromium tricarbonyl complexes (**9** and **11**) via an oxygen chelation controlled mechanism. Complexation of the t-butyldimethylsilyl protected 1-tetralol (**14**) gives a mixture of *syn*- and *anti*-diastereoisomers (**16** and **15**), with the latter favoured because the steric effect of the *O*-silyl group outweighs any chelation effect.

## Introduction

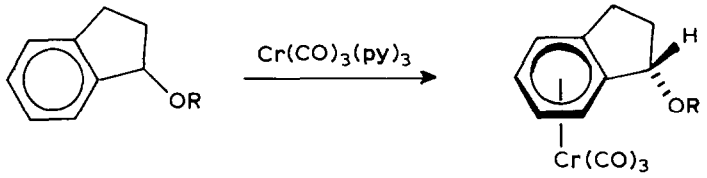
Unsymmetrical 1,2- and 1,3-disubstituted arenes are prochiral, possessing enantiotopic faces, and therefore on complexation to chromium tricarbonyl racemates are generated. The presence of a chiral centre in one of the substituents, however, renders the faces diastereotopic and therefore complexation to chromium tricarbonyl could give rise to two possible diastereoisomers but not necessarily in equal amounts. Steric effects may result in preferential complexation to one of these diastereotopic faces. For example, complexation of *N*-methyl-1-isopropyl-1,2,3,4-tetrahydroisoquinoline (**1**) to chromium tricarbonyl gives the single diastereoisomer **2** with the chromium tricarbonyl *anti* to the bulky isopropyl group [1]. Similar stereoselective complexations have been observed in other systems [2].




(**1**) (**2**)

0022-328X/88/$03.50 

It has been reported that benzylic oxygen functions can cause *syn* complexation of chromium tricarbonyl. Thus reaction of 1-indanol (**3**) or 1-methoxyindane (**4**) with (trispyridine)chromium tricarbonyl give in both cases only the *syn* chromium tricarbonyl complexes **5** and **6** respectively [3].



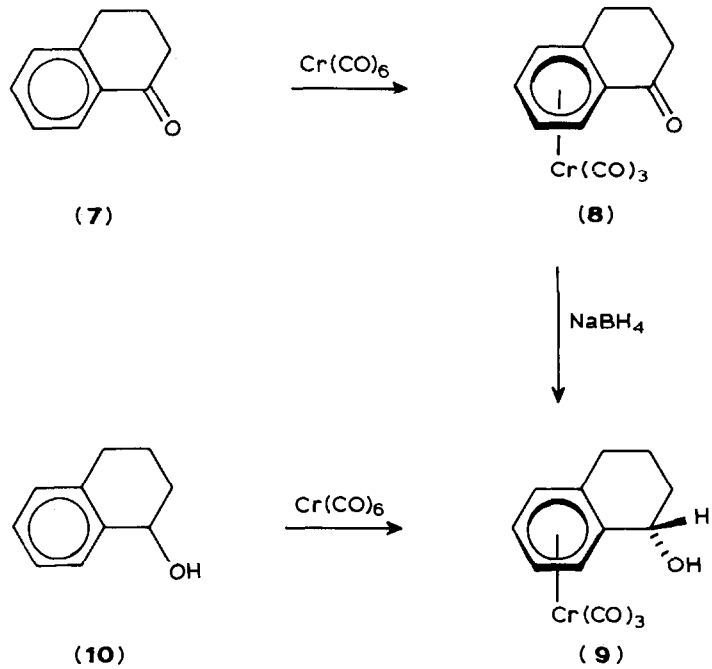

(**3**, R = H ; **4**, R = Me) (**5**, R = H ; **6**, R = Me)

A mechanism involving initial chelation of chromium to an oxygen lone pair followed by delivery to the proximate face has been invoked for these reactions [3,4]. A similar chelate mechanism would account for the predominance of the *RR,SS*-diastereoisomer in the complexation of a series of α-alkylated-2-substituted benzyl alcohols [5].

We describe here the extension of this methodology to 1-tetralol (**10**) and its derivatives **12** and **14**.

## Results and discussion

Thermolysis of chromium hexacarbonyl with 1-tetralone (**7**) gave the 1-tetralone complex **8**. Reduction of **8** with sodium borohydride in methanolic tetrahydrofuran

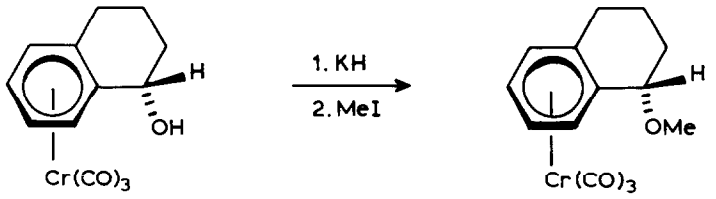



(**7**) (**8**)

(**10**) (**9**)

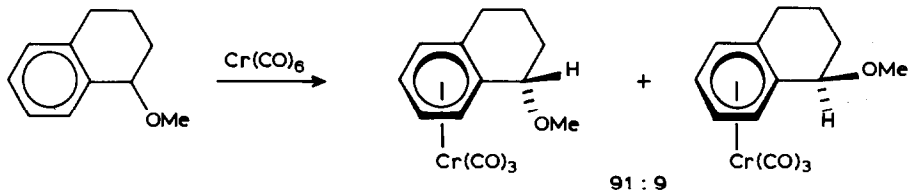
gave a single diastereoisomer of (1-tetralol)chromium tricarbonyl, assigned as the *syn* complex **9** in accord with the literature precedent [6], the ketone being reduced from the unhindered *anti* face. Thermolysis of chromium hexacarbonyl with 1-tetralol (**10**) gave *syn*-(1-tetralol)chromium tricarbonyl (**9**) as a single diastereoisomer (> 200/1). This stereoselective complexation is consistent with either chelation or hydrogen bond directed delivery of the metal moiety.

*O*-Methylation of **9** was achieved on treatment with potassium hydride followed by methyl iodide, which gave the *syn*-(1-methoxytetralin)chromium tricarbonyl complex **11** diastereoisomerically pure.




(**9**) (**11**)

Thermolysis of chromium hexacarbonyl with 1-methoxytetralin (**12**) gave the two possible diastereoisomeric complexes **11** and **13** in the ratio 91/9. The major diastereoisomer was identical to the *syn* complex **11** prepared as described above. This result is in agreement with previous findings [3], and eliminates the possibility that the stereoselective complexation of 1-tetralol (**10**) is hydrogen bond directed. The change in *syn*/*anti* stereoselectivities observed for 1-tetralol (**10**) (100/0) and 1-methoxytetralin (**12**) (91/9) is consistent with the increase in steric bulk around the coordinating oxygen.

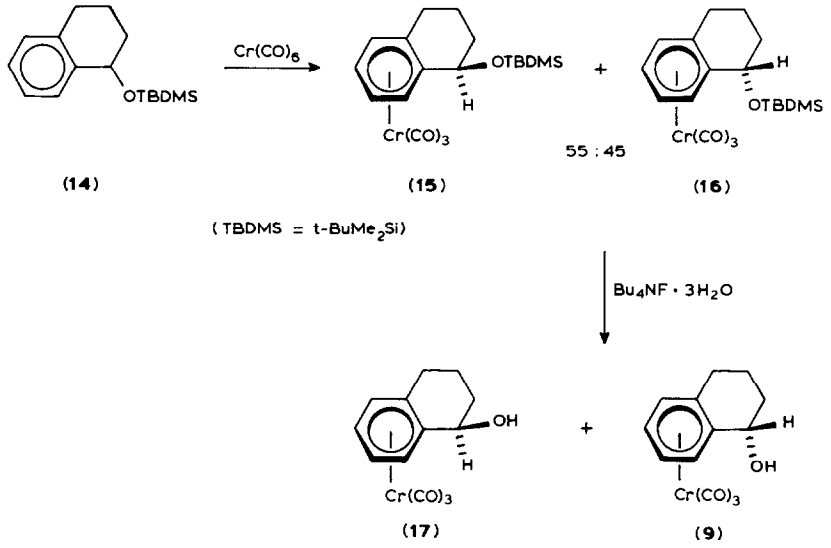



(**12**) (**11**) (**13**)

Keck [7] has shown that attachment of a $\pi$-acceptor atom, such as silicon, to oxygen decreases the ability of the oxygen to act as a Lewis base [7]. Therefore complexation of the t-butyldimethylsilyl protected 1-tetralol (**14**) should proceed with decreased *syn* selectivity. Indeed the bulky *O*-silyl group should favour complexation to the less hindered *anti* face.

1-Tetralol (**10**) was converted to **14** in good yield by treatment with imidazole and t-butyldimethylsilyl chloride in anhydrous dimethylformamide. Thermolysis of chromium hexacarbonyl with **14** resulted in complete conversion to a 55/45 mixture of the two possible diastereoisomers **15** and **16**. Partial desilylation of this mixture with tetrabutylammonium fluoride trishydrate led after chromatography to the 38% recovery of a 1/5 mixture of **15** and **16** together with the *anti*- and *syn*-1-tetralol complexes **17** and **9** in 39 and 13% isolated yields, respectively. The *syn* complex **9** was identical spectroscopically to the previously prepared sample. The depletion of **15** relative to **16** and the preponderance of **17** over **9** identify **15** unambiguously as

the *anti* diastereoisomer. Thus in the complexation of **14** to chromium tricarbonyl any remaining oxygen chelate effect is overpowered by the steric effect of the *O*-t-butyldimethylsilyl group which leads to a predominance of the *anti* isomer **15**. The greater rate of desilylation of **15** relative to **16** may be rationalised in terms of the increased steric bulk around the silicon in **16** due to its *syn* disposition relative to the chromium tricarbonyl group.




## Conclusion

The work described above has shown that the mechanism of chelation control in the stereoselective complexation of certain benzylic alcohols and derivatives occurs via a direct oxygen–metal bond. When a $\pi$-acceptor atom (Si) is bound to the oxygen normal steric preferences dominate.

## Experimental

All reactions involving (arene)chromium tricarbonyl complexes, their preparation and purification were performed under nitrogen by use of standard vacuum line techniques. DMF was distilled over calcium sulphate onto 4Å molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Diethyl ether was peroxide-free, and light petroleum refers to that fraction boiling between 60–80 °C. Dibutyl ether was dried over sodium and distilled under nitrogen, and chromium hexacarbonyl was steam distilled and dried prior to use. All commercial reagents were purified by standard techniques [8]. Column chromatography was performed on deactivated alumina (Grade V).

IR spectra were recorded as dichloromethane solutions on a Perkin–Elmer 297 instrument. $^1$H NMR spectra were recorded in chloroform-$d_1$ at 300 MHz on a

Bruker WH 300 spectrometer unless otherwise stated. 500 MHz $^1$H NMR spectra were recorded on a Bruker WH 500 spectrometer. Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. Mass spectra were recorded on a V.G. Micromass ZAB 1F or MM 30F instrument using In Beam Electron Impact techniques.

*1-(Tetralone)chromium tricarbonyl (**8**).* A mixture of dibutyl ether (45 ml), THF (5 ml), 1-tetralone (**7**) (2.00 g, 13.70 mmol) and chromium hexacarbonyl (3.92 g, 17.82 mmol) was heated under reflux (69 h). The cooled solution was filtered through Celite and evaporated. Column chromatography ($CH_2Cl_2$ as eluant) of the residue gave complex **8** as red crystals (2.57 g, 67%). $\nu_{max.}$ 1971, 1900 br (C≡O), 1682 (C=O) cm$^{-1}$; $^1$H NMR (500 MHz) $\delta$ 6.16–6.15 (d, 1H, Ar*H*), 5.64–5.62 (t, 1H, Ar*H*), 5.30–5.28 (t, 1H, Ar*H*), 5.15–5.14 (d, 1H, Ar*H*), 2.99–2.93 (m, 1H, ArC$H_2$R), 2.76–2.74 (m, 1H, ArCOC$H_2$R), 2.72–2.71 (m, 1H, ArCOC$H_2$R), 2.48–2.41 (m, 1H, ArC$H_2$R), 2.22–2.09 (m, 2H, ArCH$_2$C$H_2$R); *m/z* 282 ($M^+$).

*Reduction of 1-(tetralone)chromium tricarbonyl (**8**) with sodium borohydride [6].* To a solution of complex **8** (500 mg, 1.77 mmol) in THF (20 ml) and MeOH (5 ml) was added sodium borohydride (1.00 g, 26.40 mmol) and the mixture was stirred (2 h). It was then acidified with aqueous HCl (2 *N*) and evaporated. Column chromatography ($Et_2O$) of the residue gave *syn*-(1-tetralol)chromium tricarbonyl (**9**) as a yellow solid (409 mg, 81%). $\nu_{max.}$ 3582 (OH), 1955, 1875 br (C≡O), 1600 (arene ring) cm$^{-1}$; $^1$H NMR $\delta$ 5.85–5.83 (d, 1H, Ar*H*), 5.54–5.50 (t, 1H, Ar*H*), 5.17–5.13 (t, 1H, Ar*H*), 5.11–5.09 (d, 1H, Ar*H*), 4.53–4.51 (d, *J* 5.0 Hz, 1H, ArC*H*(OH)R), 2.81–2.71 (m, 1H, ArCH(OH)C$H_2$R), 2.65–2.56 (m, 1H, ArCH(OH)C$H_2$R), 2.15–2.08 (m, 1H, ArC$H_2$R), 2.03–1.93 (m, 1H, ArC$H_2$R), 1.78–1.61 (m, 3H, RO*H*, ArCH$_2$C$H_2$R); *m/z* 284 ($M^+$).

*Thermolysis of chromium hexacarbonyl with 1-tetralol (**10**) [6].* A mixture of dibutyl ether (50 ml), THF (5 ml), 1-tetralol (**10**) (2.00 g, 13.51 mmol) and chromium hexacarbonyl (3.86 g, 17.55 mmol) was heated under reflux (19 h). The cooled solution was filtered through Celite and evaporated. Column chromatography ($Et_2O$) of the residue gave exclusively *syn*-(1-tetralol)chromium tricarbonyl (**9**) (1.37 g, 36%) identified by comparison with an authentic sample.

*syn-(1-Methoxytetralin)chromium tricarbonyl (**11**).* A solution of complex **9** (500 mg, 1.76 mmol) in THF (8 ml) was added dropwise to a stirred suspension of KH (207 mg, 5.18 mmol) in THF (10 ml). Stirring was continued (30 min) followed by the addition of methyl iodide (1.00 g, 7.05 mmol). After further stirring (1 h) MeOH (1 ml) was added and the solution evaporated. Column chromatography ($Et_2O$) gave after recrystallisation from $CH_2Cl_2$/light petroleum complex **11** as yellow needles (429 mg, 82%). M.p. 122–124°C; $\nu_{max.}$ 2818 ($OCH_3$), 1954, 1875 br (C≡O), 1084 (C–O–C) cm$^{-1}$; $^1$H NMR $\delta$ 5.71–5.69 (d, 1H, Ar*H*), 5.42–5.38 (t, 1H, Ar*H*), 5.14–5.10 (t, 1H, Ar*H*), 5.05–5.03 (d, 1H, Ar*H*), 4.10–4.06 (m, 1H, ArC*H*($OCH_3$)R), 3.53 (s, 3H, ROC$H_3$), 2.80–2.69 (m, 1H, ArC$H_2$R), 2.62–2.53 (m, 1H, ArC$H_2$R), 2.12–1.94 (m, 2H, ArCH($OCH_3$)C$H_2$R), 1.76–1.59 (m, 2H, ArCH$_2$C$H_2$R); *m/z* 298 ($M^+$); found: C, 56.7; H, 4.8; $C_{14}H_{14}CrO_4$ calcd.: C, 56.4; H, 4.7%.

*Thermolysis of chromium hexacarbonyl with 1-methoxytetralin (**12**).* A mixture of dibutyl ether (50 ml), THF (5 ml), 1-methoxytetralin (**12**) (2.00 g, 12.35 mmol) and chromium hexacarbonyl (3.53 g, 16.05 mmol) was heated under reflux (48 h). The cooled solution was filtered through Celite and evaporated. Column chromatography ($Et_2O$) gave a mixture (ratio 91/9) of *syn*- and *anti*-(1-methoxytetralin)chro-

mium tricarbonyl (**11** and **13**) as a yellow solid (2.71 g, 74%). $^1$H NMR $\delta$ 5.71–5.69 (d, 1H, Ar*H*, **11**), 5.67–5.65 (d, 1H, Ar*H*, **13**), 5.42–5.38 (t, 1H, Ar*H*, **11**), 5.40–5.36 (m, 1H, Ar*H*, **13**), 5.28–5.24 (t, 1H, Ar*H*, **13**), 5.21–5.20 (d, 1H, Ar*H*, **13**), 5.14–5.10 (t, 1H, Ar*H*, **11**), 5.06–5.03 (d, 1H, Ar*H*, **11**), 4.18–4.15 (m, 1H, ArC*H*($OCH_3$)R, **13**), 4.10–4.06 (m, 1H, ArC*H*($OCH_3$)R, **11**), 3.53 (s, 3H, ROC$H_3$, **11**), 3.47 (s, 3H, ROC$H_3$, **13**), 2.80–2.53 (m, 4H, ArC$H_2$R, **11** and **13**), 2.14–1.56 (m, 8H, Ar$CH_2CH_2CH_2$R, **11** and **13**).

*1-t-Butyldimethylsilyltetralol (**14**).* A solution of 1-tetralol (**10**) (1.50 g, 10.14 mmol) and imidazole (830 mg, 12.21 mmol) in DMF (5 ml) was added dropwise to a cooled (0 °C) solution of t-butyldimethylsilyl chloride (1.66 g, 11.01 mmol) in DMF (5 ml) and the mixture stirred (24 h, 20 °C). Water (85 ml) was added and the solution extracted with $Et_2O$ (3 × 85 ml). The organic extracts were combined, dried ($MgSO_4$), and evaporated to leave a clear oil. Distillation gave **14** as a colourless oil (2.44 g, 92%). B.p. 96–100 °C (0.1 mm Hg); $^1$H NMR $\delta$ 7.44–7.40 (m, 1H, Ar*H*), 7.24–7.16 (m, 2H, Ar*H*), 7.11–7.08 (m, 1H, Ar*H*), 4.85–4.81 (m, 1H, ArC*H*(OR)R$^1$), 2.86–2.72 (m, 2H, ArC$H_2$R), 2.07–2.00 (m, 2H, ArCH(OR)C$H_2$R$^1$), 1.88–1.76 (m, 2H, Ar$CH_2CH_2$R), 0.99 (s, 9H, RC($CH_3$)$_3$), 0.21 (s, 3H, RC$H_3$), 0.20 (s, 3H, RC$H_3$); *m/z* 262 ($M^+$).

*Thermolysis of chromium hexacarbonyl with 1-t-butyldimethylsilyltetralol (**14**).* A mixture of dibutyl ether (50 ml), THF (5 ml), 1-t-butyldimethylsilyltetralol (**14**) (2.00 g, 7.63 mmol) and chromium hexacarbonyl (2.01 g, 9.14 mmol) was heated under reflux (75 h). The cooled solution was filtered through Celite and evaporated. Column chromatography ($Et_2O$/light petroleum 1/1) gave a mixture (ratio 55/45) of *anti-* and *syn-*(1-t-butyldimethylsilyltetralol)chromium tricarbonyl (**15** and **16**) (3.04 g, 100%). $^1$H NMR **15**: $\delta$ 5.62–5.60 (d, 1H, Ar*H*), 5.37–5.32 (t, 1H, Ar*H*), 5.29–5.24 (t, 1H, Ar*H*), 5.18–5.16 (d, 1H, Ar*H*), 4.66–4.62 (m, 1H, ArC*H*(OR)R$^1$), 2.78–2.53 (m, 2H, ArC$H_2$R), 2.05–1.90 (m, 4H, Ar$CH_2CH_2CH_2$R), 0.93 (s, 9H, RC($CH_3$)$_3$), 0.18 (s, 3H, RC$H_3$), 0.17 (s, 3H, RC$H_3$); **16**: $\delta$ 5.66–5.64 (d, 1H, Ar*H*), 5.39–5.35 (t, 1H, Ar*H*), 5.15–5.11 (t, 1H, Ar*H*) 5.07–5.05 (d, 1H, Ar*H*), 4.59–4.54 (m, 1H, ArC*H*(OR)R$^1$), 2.84–2.72 (m, 1H, ArC$H_2$R), 2.62–2.53 (m, 1H, ArC$H_2$R), 2.05–1.91 (m, 2H, Ar$CH_2CH_2CH_2$R), 1.79–1.62 (m, 2H, Ar$CH_2CH_2CH_2$R), 0.99 (s, 9H, RC($CH_3$)$_3$), 0.19 (s, 3H, RC$H_3$), 0.17 (s, 3H, RC$H_3$); *m/z* 398 ($M^+$).

*Desilylation of anti- and syn-(1-t-butyldimethylsilyltetralol)chromium tricarbonyl (**15** and **16**) mixture.* Tetrabutylammonium fluoride trishydrate (1.39 g, 4.40 mmol) was added to a mixture of complexes **15** and **16** (ratio 55/45, 1.75 g, 4.39 mmol) in THF (15 ml) and the solution stirred (8 h). Water was added (40 ml) and the aqueous mixture extracted with $Et_2O$ (3 × 40 ml). The organic extracts were combined and evaporated to a yellow solid. Column chromatography ($CH_2Cl_2$) gave three fractions. Fraction one was evaporated to a yellow solid identified by $^1$H NMR spectroscopy as a mixture (5/1) of starting complexes **16** and **15** (665 mg, 38%). Recrystallisation from $CH_2Cl_2$/light petroleum gave yellow needles of *syn-*(1-t-butyldimethylsilyltetralol)chromium tricarbonyl (**16**). M.p. 132–134 °C; $\nu_{max.}$ 1968, 1875 br (C≡O), 1600 (arene ring) cm$^{-1}$; $^1$H NMR ($C_6D_6$) $\delta$ 5.44–5.42 (d, 1H, Ar*H*), 4.62–4.58 (t, 1H, Ar*H*), 4.39–4.35 (t, 1H, Ar*H*), 4.27–4.25 (d, 1H, Ar*H*), 4.12–4.07 (m, 1H, ArC*H*(OR)R$^1$), 2.47–2.35 (m, 1H, ArC$H_2$R), 1.91–1.82 (m, 1H, ArC$H_2$R), 1.63–1.52 (m, 2H, Ar$CH_2CH_2CH_2$R), 1.49–1.36 (m, 2H, Ar$CH_2CH_2CH_2$R), 1.05 (s, 9H, RC($CH_3$)$_3$), 0.06 (s, 3H, RC$H_3$), 0.05 (s, 3H, RC$H_3$); *m/z* 398 ($M^+$); found: C, 57.4; H, 6.7; $C_{19}H_{26}CrO_4Si$ calcd.: C, 57.3; H, 6.6%. Fraction two was

evaporated to a yellow solid identified as *syn*-(1-tetralol)chromium tricarbonyl (**9**) by comparison with an authentic sample (162 mg, 13%). Fraction three was evaporated to give *anti*-(1-tetralol)chromium tricarbonyl (**17**) as a yellow oil (486 mg, 39%). $\nu_{max.}$ 3596, 3450 br (OH), 1961, 1882 br (C≡O) $cm^{-1}$; $^1H$ NMR ($C_6D_6$) $\delta$ 5.11–5.08 (d, 1H, Ar*H*), 4.47–4.43 (d of t, 1H, Ar*H*), 4.41–4.37 (d of t, 1H, Ar*H*), 4.29–4.27 (d, 1H, Ar*H*), 4.17–4.11 (q, *J* 6.0 Hz, 1H, ArC*H*(OH)R), 2.13, 1.92 ($ABX_2$ system, $J_{AB}$ 16.8 Hz, $J_{AX}$ 6.1 Hz, $J_{BX}$ 6.6 Hz, 2H, $ArCH_2R$), 1.62–1.51 (m, 1H, $ArCH_2CH_2CH_2R$), 1.42–1.21 (m, 2H, $ArCH_2CH_2CH_2R^1$), 1.15–1.04 (m, 1H, $ArCH_2CH_2CH_2R$), 1.08 (d, *J* 6.2 Hz, 1H, RO*H*); *m/z* 284 ($M^+$).

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